

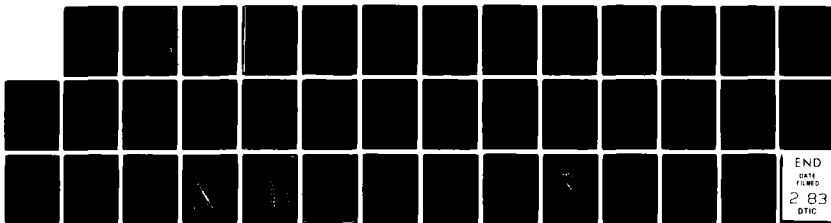
AD-A123 118

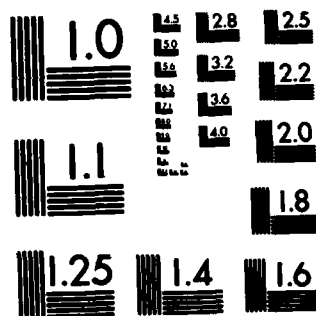
FUELS COMBUSTION RESEARCH(U) PRINCETON UNIV NJ DEPT OF 1/1  
MECHANICAL AND AEROSPACE ENGINEERING I GLASSMAN ET AL.  
30 JUL 82 MAE-1570 AFOSR-TR-82-1064 F49620-78-C-0004

UNCLASSIFIED

F/G 21/2

NL





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>AFOSR-TR- 82-1064</b>	2. GOVY ACCESSION NO. <b>AD-A123118</b>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) <b>FUELS COMBUSTION RESEARCH</b>		5. TYPE OF REPORT & PERIOD COVERED <b>FINAL</b> <b>1 Oct. 78 - 30 Sept. 81</b>
7. AUTHOR(s) <b>I. GLASSMAN</b>		6. PERFORMING ORG. REPORT NUMBER <b>1570-MAE</b>
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>PRINCETON UNIVERSITY</b> <b>DEPARTMENT OF MECHANICAL &amp; AEROSPACE ENGINEERING</b> <b>PRINCETON, NEW JERSEY 08544</b>		8. CONTRACT OR GRANT NUMBER(s) <b>F49620-78-C-0004</b>
11. CONTROLLING OFFICE NAME AND ADDRESS <b>AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA</b> <b>BLDG. 410</b> <b>BOLLING AIR FORCE BASE, D.C. 20332</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <b>2308/A2</b> <b>61102F</b>
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE <b>July 1982</b>
		13. NUMBER OF PAGES <b>22</b>
		15. SECURITY CLASS. (of this report) <b>Unclassified</b>
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) <b>Approved for public release; distribution unlimited.</b>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <b>CHEMICAL KINETICS</b> <b>TURBULENT FLOW REACTOR</b> <b>HYDROCARBON FUELS</b> <b>OXIDATION KINETICS</b> <b>SOOT FORMATION</b> <b>AROMATIC OXIDATION</b> <b>CARBON OXIDATION</b> <b>HYDROCARBON PYROLYSIS</b>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>Because propane is the simplest hydrocarbon which exhibits characteristics similar to those of more complex fuels, a thorough study of the pyrolysis and oxidation of propane was undertaken in the Princeton turbulent flow reactor. The pyrolysis rate was found to first order with respect to the fuel with a pre-exponential factor of <math>3.2 \times 10^{12.5}</math> and activation energy of 86.65 kcal/mole. A detailed mechanism was developed which fits a wide range of data and indicates that the literature values for the rate constant for the reaction methyl plus propane would be in error. This and earlier work with hydro-</b>		

AD A123118

DTIC FILE COPY

DTIC  
ELECTE  
JAN 7 1983  
12.5  
E

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

carbon oxidation provided the means for developing an overall kinetic scheme for all aliphatic hydrocarbon oxidation which would accurately predict major species formed and the temperature-time history (rate of heat release) of the reaction. The work is of great importance to the field of combustor modelling since the overall scheme involves only four reactions: conversion of the aliphatic fuels to ethylene, the oxidation of ethylene to CO, and the conversion of CO and H<sub>2</sub> to CO<sub>2</sub> and H<sub>2</sub>O.

One of the first high temperature mechanisms for the oxidation of aromatic fuels has been proposed after extensive flow reactor studies with benzene, toluene and ethyl benzene. The controlling factor in all three studies is the rate of oxidation of the phenyl radical initially formed in each case. With the new realization that phenyl plus O<sub>2</sub> was an exothermic, relatively rapid chain-branching reaction, the mechanism and extensive data indicate the route of conversion is phenoxy, ketocyclohexadienyl, cyclopentadienyl, butadienyl, vinyl acetylene, butadiene, acetylene and vinyl radicals. CO is expelled from the ring structures to give the next lower order hydrocarbon and is the reason CO is found early in aromatic flames. More importantly however is that the similarity of the mechanisms for the three fuels holds high hopes for an overall kinetic model such as that developed for aliphatics. Further the discovery of vinyl acetylene and butadiene as intermediates gives a further clue to reason for the extensive sooting characteristics of aromatic fuels.

Studies on soot formation in combustion systems led to the postulate that vinyl acetylene and butadiene, essentially C<sub>4</sub> conjugated compounds, could be the key precursors in soot formation and that the controlling factor in the amount of soot found in both pre-mixed and diffusion flame combustion system was the rate of pyrolysis of the fuel. The general classification of the tendency of classes of fuels to soot reported in the literature was found to be incorrect due to the omission of the role of the flame temperature. The sooting tendency in pre-mixed flames is determined by two competing factors: the rate of increase of soot precursor formation with temperature and the rate of increase of oxidative attack on these precursors. Since the oxidative attack increases faster, the higher the temperature the less the tendency to soot. Since in diffusion flames there is no oxidative attack, the higher the temperature the tendency to soot is greater. Extensive experimental work is reported to support these considerations. Liquid pool sooting height studies of fuel mixtures revealed the important fact that 20% aromatics in a fuel soots about as if the fuel were purely aromatic.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

**AFOSR-TR- 82 - 1064**


**Final Report Under AFOSR Contract  
F49620-78-C-0004  
Air Force Office of Scientific Research**

**FUELS COMBUSTION RESEARCH**

**For the Period 1 October 1978 to 30 September 1981**

**Profs. I. Glassman and F.L. Dryer, Co-Principal Investigators**

Prepared by

  
Irvin Glassman  
Professor  
Co-Principal Investigator  
Correspondant

30 July 1982

School of Engineering and Applied Science  
Department of Mechanical and Aerospace Engineering  
Princeton University  
Princeton, New Jersey 08544

Report No. 1570-MAE

**88 01 07 046**

Approved for public release;  
distribution unlimited.

## Abstract

The significant results of the Fuels Combustion Research Program at Princeton supported by AFOSR for the period 1 October 1978 to 30 September 1981 are the subject of this final report for Contract F49620-78-C-0004.

Because propane is the simplest hydrocarbon which exhibits characteristics similar to those of more complex fuels, a thorough study of the pyrolysis and oxidation of propane was undertaken in the Princeton turbulent flow reactor. The pyrolysis rate was found to first order with respect to the fuel with a pre-exponential factor of  $3.2 \times 10^{12.5}$  and activation energy of 86.65 kcal/mole. A detailed mechanism was developed which fits a wide range of data and indicates that the literature values for the rate constant for the reaction methyl plus propane would be in error. This and earlier work with hydrocarbon oxidation provided the means for developing an overall kinetic scheme for all aliphatic hydrocarbon oxidation which would accurately predict major species formed and the temperature-time history (rate of heat release) of the reaction. The work is of great importance to the field of combustor modelling since the overall scheme involves only four reactions: conversion of the aliphatic fuels to ethylene, the oxidation of ethylene to CO, and the conversion of CO and H<sub>2</sub> to CO<sub>2</sub> and H<sub>2</sub>O.

One of the first high temperature mechanisms for the oxidation of aromatic fuels has been proposed after extensive flow reactor studies with benzene, toluene and ethyl benzene. The controlling factor in all three studies is the rate of oxidation of the phenyl radical initially formed in each case. With the new realization that phenyl plus O<sub>2</sub> was an exothermic, relatively rapid chain-branching reaction, the mechanism and extensive data indicate the route of conversion is phenoxy, ketocyclohexadienyl, cyclopentadienyl, butadienyl, vinyl acetylene, butadiene, acetylene and ~~vinyl radicals~~. CO is expelled from

AFOSR OFFICE OF SCIENTIFIC RESEARCH (AFSC)  
NOTICE OF TRANSMITTAL TO DTIC  
This technical report has been reviewed and is  
approved for release IAW AFR 190-12.  
Distribution is unlimited.  
MATTHEW J. MEYER  
Chief, Technical Information Division

the ring structures to give the next lower order hydrocarbon and is the reason CO is found early in aromatic flames. More importantly however is that the similarity of the mechanisms for the three fuels holds high hopes for an overall kinetic model such as that developed for aliphatics. Further the discovery of vinyl acetylene and butadiene as intermediates gives a further clue to reason for the extensive sooting characteristics of aromatic fuels.

Studies on soot formation in combustion systems led to the postulate that vinyl acetylene and butadiene, essentially C<sub>4</sub> conjugated compounds, could be the key precursors in soot formation and that the controlling factor in the amount of soot found in both pre-mixed and diffusion flame combustion system was the rate of pyrolysis of the fuel. The general classification of the tendency of classes of fuels to soot reported in the literature was found to be incorrect due to the omission of the role of the flame temperature. The sooting tendency in pre-mixed flames is determined by two competing factors: the rate of increase of soot precursor formation with temperature and the rate of increase of oxidative attack on these precursors. Since the oxidative attack increases faster, the higher the temperature the less the tendency to soot. Since in diffusion flames there is no oxidative attack, the higher the temperature the tendency to soot is greater. Extensive experimental work is reported to support these considerations. Liquid pool sooting height studies of fuel mixtures revealed the important fact that 20% aromatics in a fuel soots about as if the fuel were purely aromatic.

## Table of Contents

Abstract

### Table of Contents

I.	Introduction.....	1
II.	Hydrocarbon Oxidation and Pyrolysis Mechanisms.....	1
-	A. Pyrolysis of Propane.....	2
	B. General Aliphatic Fuel Oxidation Mechanisms.....	3
	C. Application to Sooting in Premixed Flames.....	4
	D. An Overall Kinetic Mechanism for the Oxidation of Aliphatic Hydrocarbon Fuels.....	4
	E. Oxidation of Aromatic Fuels.....	7
III.	Soot Formation in Premixed and Diffusion Flame Combustion Systems.....	9
	A. Sooting Diffusion Flame Combustion Systems.....	11
	B. Premixed Combustion Systems.....	14
IV.	References.....	16
V.	Student, Post-Doctoral and Visitor Training.....	20
VI.	Publication Interest.....	21
	List of Figures.....	22

## **I. INTRODUCTION**

The AFOSR supported research at Princeton for the period 1 October 1978 to 30 September 1981 is the subject of this final report. The Princeton program focussed on chemically related fuel combustion problems and primarily dealt with the pyrolysis and oxidation mechanisms of aliphatic and aromatic hydrocarbon fuels, the development of kinetic models to aid in the computer modelling of combustion chambers and soot formation processes. Considering that fuel stocks at Air Force bases are containing higher percentages of aromatics and are showing worse smoke point results, the results obtained in this program are thought to be directly pertinent to the solution of an important Air Force problems.

## **II. HYDROCARBON OXIDATION AND PYROLYSIS MECHANISMS**

This section will include all the work on kinetic mechanisms and modelling and the next section will include all the work on soot formation. The order of discussion will be oxidation and pyrolysis of aliphatic hydrocarbons, overall modelling of aliphatic mechanisms and oxidation of aromatics. Although some of the work on oxidation was completed prior to initiation of the contract which this report covers, the results of the earlier program were important to reaching significant conclusions with respect to the research for the period covered and will thus be reviewed in that context here.

### **Aliphatic Hydrocarbon Fuel Mechanism**

All the kinetic mechanisms were derived from the experimental results obtained with the Princeton turbulent flow reactor developed under AFOSR sponsorship. This reactor shown in Figure 1 has been described in previous publications (see Ref. 1) and is unique as compared to other chemical kinetic reactors. The gas mixture is mainly nitrogen which is heated by a plasma torch. A small amount of oxygen is injected prior to the mixing nozzle and

the fuel in gaseous form is injected at the throat of the nozzle. When fuel pyrolysis alone is studied, no oxygen is injected. The total velocity of the gas mixture is great enough and the total length of the reactor long enough to ensure the existence of fully developed turbulent flow in the reactor zone. As a result the fluid mechanics are able to be characterized as 1-dimensional or plug-flow and the transformation from distance to time becomes very straightforward. Another consequence of this turbulent condition is that samples can be drawn from the centerline alone. Since only a small amount of fuel is injected, longitudinal gradients of reactive species are very small and the amount of energy release is limited. These conditions, when coupled with large convective flow in the reactor, result in longitudinal diffusion of mass and energy being negligible. The reactor is large enough to eliminate wall effects and is electrically heated to make the reactor adiabatic.

Essentially the flow reactor spreads a laminar flame reaction system which is normally 1 millimeter thick over a 1 meter region and eliminates the large diffusion corrections necessary to extract kinetic results from flames.

#### A. Pyrolysis of Propane

Most of the early results on the oxidation of aliphatic hydrocarbons were reported in Reference 1 and many contributions to the fundamental chemical kinetic literature were made [2,3,4]. The primary fundamental results during the contract period which this report covers were concerned with the pyrolysis of propane [5,6]. Such results are important, because from a combustion point of view, propane is the simplest hydrocarbon which exhibits characteristics similar to those of the more complex fuels [1].

Extensive flow reactor data over the temperature range 1110-1235 and at 1 atm suggested that the overall pyrolyses rate could be represented by the expression

$$\frac{d(C_3H_8)}{dt} = 3.2 \times 10^{12.5 \pm 0.34} \exp[(-58,650 \pm 1800)/RT] (C_3H_8)$$

where the units are cgs. In addition a kinetic mechanism involving 13 chemical species and 32 elementary reactions was postulated to describe the detailed kinetics [5]. This mechanism was found to agree with the results from static vessel and shock tube experiments of others as well as our flow reactor results. Agreement over the temperature range 800-1400 K and over the pressure range of 0.1-8.5 atm was obtained by adjusting three rate constants. Previously reported values for these rate constants appear to require reexamination in light of our work. The reactions in question are the following:



The sum of the rate constants for Reactions (a) and (b) and the rate constant for Reaction (c) are best represented by

$$k_a + k_b = 10^{-0.1} T^4 \exp(-8300/RT) \text{ cm}^3/\text{mol sec}$$

$$k_c = 10^{14.55} \exp(-14,340/RT) \text{ cm}^3/\text{mol sec}$$

which differ from previous report values.

## B. General Aliphatic Fuel Oxidation Mechanisms

From a combustion point of view the most significant finding was that during oxidation all paraffin hydrocarbons broke down to the three lowest olefins (ethylene, propylene and butylene) and then the olefins were oxidized to CO, which was subsequently oxidized to CO<sub>2</sub>. Ethylene is normally the dominant olefin so one can conclude that the oxidation of all aliphatics boils down to the oxidation of ethylene. A good example of this phenomenon is represented by the flow reactor results on the oxidation of octane shown in Figure 2.

This important generalization with respect to the oxidation of aliphatic

fuels gave pertinent clues to modelling techniques and the understanding of soot formation under premixed flame conditions such as those which can exist in the primary zone of an aircraft gas turbine combustion chamber.

#### C. Application to Sooting in Premixed Flames

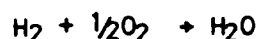
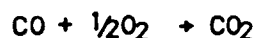
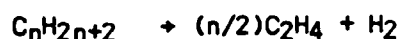
First the application to the soot problem will be considered. When the oxidizer to fuel ratio in the flow reactor was controlled so that the system was fuel rich, significant amounts of acetylene were found, as shown in Figure 3. If the oxidation of aliphatic fuels followed the route through the lower olefin, ethylene, and under rich conditions the ethylene degraded further to acetylene, then the generally accepted sooting trend that paraffins had a greater tendency to soot than olefins and the olefins a greater tendency to soot than acetylene, could not be correct. If all aliphatics under rich conditions pyrolyze to a degree to acetylene, then acetylene should be the most prolific sooting fuel. It will be shown later that acetylene appears to soot less under premixed conditions because of its high adiabatic flame temperature.

#### D. An Overall Kinetic Mechanism for the Oxidation of Aliphatic Hydrocarbon Fuels

Modern engineering practice has led to computer modelling of combustion chambers as the first step in engine development. Computer models exist for the design of aircraft gas turbine combustors, catalytic combustion chambers and spark-ignited and diesel automotive engines. The complexity of these models depend on the dimensionality chosen for the fluid mechanical processes and the extent to which the chemistry of the combustion process is to be described. The models best approach reality usually with a 2 or 3 dimensional turbulent flow pattern. To impose complex chemical kinetic combustion details on what is already a complex fluid mechanical problem makes the solution of

the problem a formidable and expensive task. The modeller needs a simplified chemical kinetic mechanism which will properly describe the important intermediates and final products and the rate of energy release. We believe the program during the subject contract period has been successful in this regard for aliphatic fuels.

The essential clue to the modelling was the finding just discussed, that in the oxidation process, all fuels were converted to the lower olefins which were then oxidized. The proposed overall mechanism follows the general form [6,7]:



where  $C_2H_4$  represents a class of olefinic intermediates which are known to be primarily ethene and propene. The corresponding rate expressions, developed primarily from propane oxidation results, are

$$\frac{d[C_nH_{2n+2}]}{dt} = 10^x \exp(-E/RT) [C_nH_{2n+2}]^a [O_2]^b [C_2H_4]^c \text{ mole/cc-s} \quad (I)$$

$$\frac{d[C_2H_4]}{dt} = 10^x \exp(-E/RT) [C_2H_4]^a [O_2]^b [C_nH_{2n+2}]^c \text{ mole/cc-s} \quad (II)$$

$$\frac{d[CO]}{dt} = \{-10^x \exp(-E/RT) [CO]^a [O_2]^b [H_2O]^c\} \times S \text{ mole/cc-s} \quad (III)$$

$$\frac{d[H_2]}{dt} = 10^x \exp(-E/RT) [H_2]^a [O_2]^b [C_2H_4]^c \text{ mole/cc-s} \quad (IV)$$

where the parameters for I are  $x = 17.32 \pm 0.68$ ,  $E = 49,600 \pm 2400$ ,  $a = 0.50 \pm 0.02$ ,  $b = 1.07 \pm 0.05$ , and  $c = 0.40 \pm 0.03$ ; for II,  $x = 14.70 \pm 2.00$ ,  $E = 50,000 \pm 5000$ ,  $a = 0.90 \pm 0.08$ ,  $b = 1.18 \pm 0.10$ , and  $c = -0.37 \pm 0.04$ ; for IV,  $x = 13.52 \pm 2.2$ ,  $E = 41,000 \pm 6400$ ,  $a = 0.85 \pm 0.16$ ,  $b = 1.42 \pm 0.11$ , and  $c = -0.56 \pm 0.20$ ; and for III,  $x = 14.6 \pm 0.25$ ,  $E = 40,000 \pm 1200$ ,  $a = 1.0$ ,  $b =$

0.25, and  $c = 0.50$ .  $S = 7.93 \exp(-2.48\phi)$ , where  $\phi$  is the initial equivalence ratio and  $S$  cannot take values greater than 1.

Examination of the many flow reactor profiles revealed that the fuel initially increases in its rate of decay and then slows down. A simple rate expression containing fuel and oxygen concentrations only would show a constant decreasing value. It was noted that as the radical pool built up so did the formation of the olefin, the olefin would compete with the fuel for radicals and then decay. Thus the olefin concentration was a good measure of the radical pool available for fuel attack. It increased and then decreased. Thus the olefin concentration was added to Rate Equation I. The fuel olefin competition then demanded the addition of the fuel concentration to the olefin Rate Equation II, but now the power (or order) of the fuel concentration must be negative because the fuel is an inhibitor to the olefin oxidation by its competition for radicals. The CO oxidation rate expression is the same as that originally recommended by Dryer and Glassman [8], except that a correction factor for rich conditions has been added. Most of Dryer and Glassman's early work on CO was for lean operation. The modification to the hydrogen oxidation Rate Equation IV is of the form to account for the competition of oxidizing radicals between the hydrogen and olefin.

The rate expressions were found to predict within reasonable accuracy flow reactor and shock tube results on propane oxidation which encompass an equivalence ratio range 0.12 to 2.0, a temperature range 960 to 1540 K and a pressure range 1 to 9 atms. With minor modification, experimental flow reactor results on the oxidation of butane, 2- and 3- methyl pentane, and n-octane are also predicted. Shown in Figure 4 is the agreement between the predicted and actual flow reactor experimental results for butane oxidation.

### E. Oxidation of Aromatic Fuels

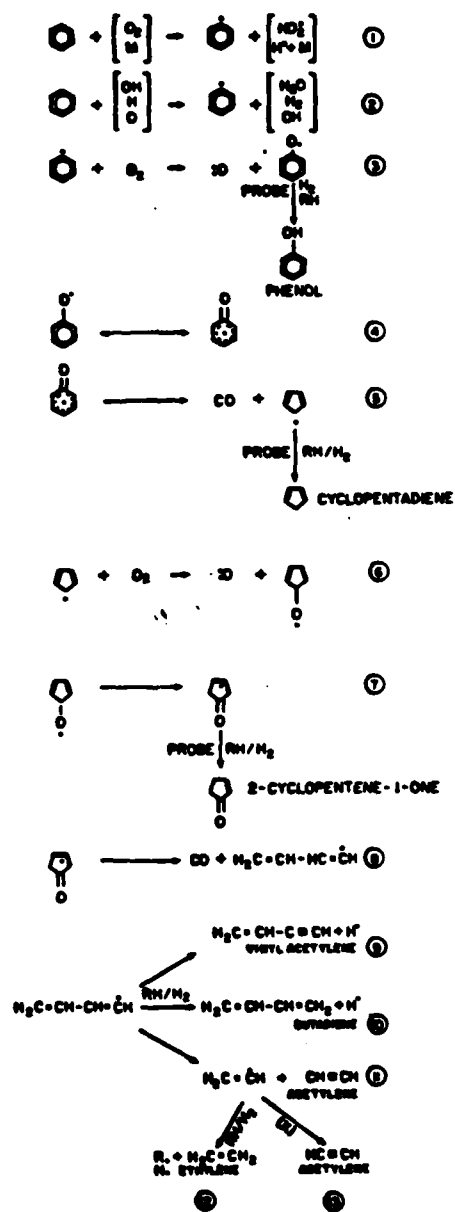
The ability to burn highly aromatic fuels and the general tendency of such fuels to form deleterious amount of soot and coke particles made it evident that an understanding of the detailed homogeneous oxidation kinetics was necessary. Coupled with the fact that aircraft fuels always contain aromatics, irrespective of degree, it was evident that such understanding was necessary to provide overall rate expression for those engaged in computer modelling and design of combustion chambers as discussed previously.

Early review [9] of the literature revealed little information on the possible high temperature aromatic oxidation mechanisms and our early experimental results with toluene [10,11] in the flow reactor in this program made it evident that the mechanisms in the literature proposed for low temperatures were not appropriate for the high temperature regimes of combustion. Subsequently we studied and are currently studying on a follow-up AFOSR program, the oxidation of benzene, toluene and ethyl benzene. The interesting results obtained and reported [12,13] indicated that the three aromatics were oxidized in the same fashion once the alkyl group in toluene and ethyl benzene had been oxidized. Essentially they are similar in that all three oxidation rates appeared to be controlled by the oxidation of the phenyl radical which forms in each case. For purposes here we will not discuss the oxidation of the alkyl side chain in the cases of toluene and ethyl benzene as the details are reported elsewhere [12,13], but will concentrate on the oxidation of benzene and its radical, phenyl. Shown in Figure 5a,b,c,d are actual flow reactor results for the lean ( $\phi = 0.39$ ) oxidation of benzene at an initial temperature 1130 K and 1 atm pressure. There are many important and interesting features to be observed from these typical flow reactor results. In Figure 5a, the benzene ( $C_6H_6$ ) is readily observed and the important intermediate found is

phenol ( $C_6H_5OH$ ), which is essentially the phenoxy radical ( $C_6H_5O$ ) since only stable species can be determined due to the sampling techniques [10] used for gas chromatographic and mass spectrographic analyses. CO is found to form earlier in the reaction system than that observed for aliphatic compounds (see Figure 2). Figure 5b shows that the sequence of major species to be: cyclopentadiene ( $C_5H_6$ ), vinyl acetylene ( $C_4H_4$ ), butadiene ( $C_4H_6$ ), and some  $C_3$  hydrocarbons. Figure 5d shows that subsequently acetylene ( $C_2H_2$ ), ethylene ( $C_2H_4$ ) and methane ( $CH_4$ ) form. Figure 5c shows the temperature rise (energy release) and its close correspondence to the CO and  $CO_2$  conversion (compare Figure 5a and Figure 5c). These results, and similar ones for toluene led us to propose the following mechanism for benzene (in reality phenyl radical) oxidation (see Table I).

Benzene oxidation is initiated by either oxidative abstraction of a hydrogen to form the phenyl radical or simple pyrolysis (Reaction 1). Once this radical pool is formed the phenyl radicals are formed by radical abstraction (Reaction 2). The realization that phenyl plus  $O_2$  was exothermic (Reaction 3) was a major contribution in determining the remaining part of the mechanism. This reaction results in the phenoxy radical, which appears in the probe as phenol. Work on phenol pyrolysis reported in the literature revealed the isomerization of phenoxy to ketocyclohexadienyl (Reaction 4) and the subsequent expulsion of CO from ketocyclohexadienyl to form the cyclopentadienyl radical (Reaction 5). We then propose that the cyclopentadienyl radical is oxidized similarly to the phenyl radical to form a reaction product (Reaction 6) which quickly isomerizes to a ketone radical (Reaction 7) whose stable form in the probe is 2-cyclopentene-1-one. The cyclopentenoxyl radical is expected to once again follow the ring rupture step of CO expulsion to form as well the butadienyl radical (Reaction 8). The fate of the butadienyl radical is repre-

TABLE I  
BENZENE OXIDATION: PROPOSED MECHANISM



sented by Reactions 9-13, but the very important element is that it forms vinyl acetylene, butadiene, vinyl radical (Reaction 11) and acetylene, all of which we had earlier postulated to be of importance is soot formation.

Thus it would appear that the aromatics form soot readily not only due to their original structure but also to the fact they form the other important precursors. Since the rate and mechanism of formation of these precursors (essentially vinyl acetylene and butadiene) is different than that obtained with aliphatic fuels (and certainly faster), then as we will see in a subsequent section the aromatics should have a greater propensity to soot than the aliphatics. Presently it is not known whether this rate of formation with respect to temperature is faster, slower or equal to the rate of oxidative attack on them. Thus for aromatic fuels under premixed conditions it is presently not known whether the sooting tendency decreases with rising temperature or not. This aspect is one element of our present AFOSR research.

### III. SOOT FORMATION IN PREMIXED AND DIFFUSION FLAME COMBUSTION SYSTEMS

The results obtained in this part of the program have had a lasting impact on national and international research efforts in the field of soot formation processes. Over 500 copies of AFOSR Report No. 79-1147 "Phenomenological Models of Soot Formation in Combustion Systems" [14] were distributed, mostly to accommodate external requests. The major new concepts which developed in the program were as follows. The general ideas that a polyacetylene route to soot nucleation could not be correct [14] and that a mechanism that required the formation of conjugated species such as butadiene and vinyl acetylene that could possibly undergo Diels-Alder type reactions was more likely. Although normal Diels-Alder type reaction may still not be fast enough, certain ions of butadiene could undergo such fast reactions. Thus this idea molds with concepts put forth by Calcote [15] in a somewhat dif-

ferent manner. Perhaps the more important concept is that fuel pyrolysis rates (and not the rate of nucleation) control the rate of soot formation. This postulate stems from some early work of Millikin [16], whose results were never properly emphasized. Millikin, whose work was on premixed ethylene-air flames only, simply stated that the rate of soot formation under premixed conditions was determined by the competition of the rate of formation of the soot precursors and the rate of oxidative attack on these precursors. Since the oxidative attack increases with temperature faster than the formation rate, the higher the temperature under premixed conditions, the less the tendency to soot. Since there is no competitive oxidative attack in diffusion flames, they soot more extensively the higher the stoichiometric temperature. Thus we pointed out the important role of flame temperature in determining sooting propensity. Lastly, the early evidence [17] that butadiene and vinyl acetylene were prolific sooting fuels and the fact that these compounds could possibly undergo particularly fast organic association reactions at high temperature led us to postulate that the C<sub>4</sub> and possibly C<sub>5</sub> conjugated species (di-olefins and higher acetylenes) were unique in their sooting quality. Obviously early work [17] indicated aromatic fuels had the same quality. Thus fuel structure (and not hydrogen content) was proposed as an important element to soot formation.

These conceptual ideas which developed from our literature search and early experimental results led us to question the generally accepted categorization that the tendency to soot in premixed flames followed the order [18,19]

aromatics > alcohols > paraffins > olefins > acetylene  
and in diffusion flames followed the order [17,19]

aromatics > acetylenes > olefins > paraffins > alcohols.

Except for the aromatics, this categorization for the homologous organic fuel

series following our postulated trend that for premixed flames the higher the flame temperature the less the tendency to soot and for diffusion flames, vice-versa. The kinetic work on aromatics discussed in Section IIE shows that this class of compounds oxidatively pyrolyzes differently than the aliphatic fuels and more importantly during its pyrolyses step forms butadiene and vinyl acetylene, other important precursors to soot. Indeed there may be synergistic effect of these compounds with aromatic structures to form soot and this synergism may be the reason aromatics have such a great tendency to soot.

#### A. Diffusion Flame Combustion Systems

Another experimental part of the program was to verify these concepts. Most of these efforts during the three year period of concern here was directed at diffusion flames, although some premixed flame data will be reported. The general means of evaluating the tendency of fuels to soot is by the so-called ASTM smoke point test [20]. The apparatus developed was a precise method of creating a highly overventilated laminar gaseous fuel jet flame. It consisted of a 1 cm fuel jet surrounded by a 10 cm concentric oxidizing (generally air) stream. Whereas the ASTM test burns liquids on a wick, in these controlled experiments, liquid fuels were vaporized. Further many have obtained spurious results by not operating in the highly overventilated regime [21]. There have been others [17] who performed similar experiments and the results obtained follow the trend we have criticized; however no other investigator had controlled the diffusion flame temperature. Temperature control was obtained by the simple addition of inerts to the fuel jet. We had shown through extensive experimentation [22] that addition of inerts did not alter the diffusion flame height as simple diffusion flame theory predicts [19]. The height of a laminar diffusion flame is proportional to the flow

rate of the fuel alone!!

The smoke point of a fuel is obtained by increasing the fuel jet flow rate until a soot streak breaks the smooth, continuous, laminar, luminous flame front. The flame height at this condition is the smoke point and data are reported as either smoke point, or mass or volumetric flow rate of fuel at the smoke point. The mass flow rate is the best parameter since it normalizes the data with respect to number of carbon atoms in the fuel. When the normal smoke point is reached, an inert diluent is added and the soot streak disappears. The flow rate of the fuel must be increased until another smoke point is reached. More diluent is added, the fuel flow rate increased, etc. Thus the smoke point varies with the amount of diluent added, or more exactly, with the inner stoichiometric flame temperature which is controlled by the amount of diluent. One may then plot the smoke point, or mass flow rate at the respective smoke point, as a function of the calculated adiabatic, stoichiometric, flame temperature. However our initial postulate was that fuel pyrolysis rates were the controlling factor in the tendency to soot. If this postulate were true, then the smoke height would be a measure of the rate of pyrolysis of the fuel. The higher the smoke point, the less is the tendency to soot. Then the inverse of the smoke point, or the inverse of the mass flow rate of the fuel, is a measure of the pyrolysis rate. Since pyrolysis rates follow Arrhenius kinetics, then it was postulated that a plot of the logarithm of the inverse of the rate versus  $1/T$  should give straight lines [21,22]. Figure 6 shows the results for over ten fuels and all indeed fall on a straight line. The highest temperature point for each fuel, except for ethylene, is the result for no dilution or temperature control. Ethylene was preheated to show that the inert had no other effect.

There are many interesting conclusions to be drawn from Figure 6. Most

obvious is the importance of flame temperature and the ancillary reasoning that the fuel pyrolysis rate must be a significant, if not controlling factor, in soot formation. At a fixed temperature note that acetylene soots less than many olefins. Examining the olefins results carefully shows that the C<sub>4</sub> and C<sub>5</sub> olefins have the greatest tendency to soot amongst this homologous fuel series. These results are consistent with the conceptual ideas put forth earlier [14] and show the importance of fuel structure. The aromatics are seen to have the greatest tendency to soot and there does not appear to be a great difference in the sooting tendency of the various aromatic compounds, which is consistent with our aromatic kinetic results that the process may be controlled by what happens to the phenyl radical even in pyrolysis. More work on aromatics, and other conjugated fuel structures, and the measuring of the slopes in Figure 7 is currently in progress on a follow-up AFOSR contract.

Some other type diffusion flame work was completed at the beginning of the subject program and is very significant from an Air Force point of view. A liquid diffusion flame apparatus was built [24,25], not based on a wick procedure as the ASTM test, but by controlling the flame height by varying the diameter of the liquid pool. Various liquid fuel mixtures were tested and the significant findings are represented in Figure 7. Notice in the figure that there is a linear variation of smoke point for aliphatic fuel mixtures, but not so for an aromatic-aliphatic mixture. The data indicate that a fuel containing around 20% aromatics will smoke as much as a pure aromatic fuel!

In the gaseous fuel jet experiments the temperature was varied by the addition of an inert to the fuel. Another means of varying the temperature is by controlling the oxygen-nitrogen ratio (so-called oxygen index) of the concentric oxidizing stream. Experimentation in the program showed that different effects could be obtained. When an inert is added to the fuel jet, the

whole temperature profile in the fuel pyrolysis zone changes. When the oxygen-index changes, the flame temperature changes and so does the burn-up of particles at the flame zone. Variation of smoke point with oxygen index is shown in Figure 8. These data show that the smoke point reaches a maximum, minimum sooting tendency, around an oxygen index of 0.23. This maximum is due to two competing effects with different temperature dependencies [21,26]. At low oxygen concentrations the rate of particle burn-up proceeds faster than the rate of particulate formation. At higher temperature, the opposite condition prevails. One may come to an important conclusion from our results on oxygen index work and that it is more effective to control the particulate formation to reduce soot exhaust than it is to attempt particulate burn-up.

#### B. Premixed Combustion Systems

Returning now to sooting conditions for premixed systems, such as may exist in the primary zone of an aircraft gas turbine combustion chamber, the temperature effect proposed was also examined experimentally [27,29]. The sooting tendency under pre-mixed conditions is determined by varying the equivalence ratio of a premixed laminar flame until luminosity is observed in the flame. The luminosity arises from the formation of soot. The larger the equivalence ratio, that is the more fuel-rich condition, necessary to cause luminosity, the less the tendency to soot. As discussed earlier, it had been reported [18] that the tendency to soot under premixed conditions followed the order paraffins > olefins > acetylene. This order was inconsistent with the kinetic results obtained in this program and the trend actually followed was postulated to be an effect of the temperature at the mixture ratio created, rather than the fuel structure. Thus a laminar Bunsen cone apparatus similar to that of Street and Thomas [18] who produced much of the early work was constructed. The experimentation which followed however was different from all

earlier work in that the temperature was controlled by using various oxygen-nitrogen mixtures to vary the temperature at a given equivalence ratio. All earlier experimentation was only with air. The results obtained verified the concepts put forth. Shown in Figure 9 are some of these results on ethane, ethylene and acetylene, which are an improvement over similar data reported earlier [27]. This effort is continuing in the current Air Force program [28]. In Figure 9, the data points with crosses are the results obtained with air and agree with those reported by Street and Thomas [18] and support the trend they reported earlier. However, one quickly sees that at a fixed temperature, the acetylene soots at a lower equivalence ratio than the ethylene and ethane as our kinetic results suggested. Thus if the primary zone of an aircraft gas turbine combustion truly acts as a premixed stirred reactor, then to reduce particulate formation it is best to operate at the highest temperature possible if the fuel is primarily aliphatic in nature. Our current Air Force program is examining what the specific trends are when aromatics are used.

#### IV. REFERENCES

\*\* Publications Under Subject AFOSR Contract

\* Publications Under Previous AFOSR Contracts

- \*\* 1. Dryer, F.L. and Glassman, I., "Combustion of Chain Hydrocarbons", in "Alternate Hydrocarbon Fuels: Combustion of Chemical Kinetics", Vol. 62, Progress in Aeronautics and Astronautics, Amer. Inst. of Aero. and Astro., New York, p. 255 (1978).
- \* 2. Schug, K.P., Santoro, R.J., Dryer, F.L. and Glassman, I., "An Investigation of the Pyrolysis and Oxidation of Ethylene in a Turbulent Flow Reactor", Western States Section/The Combustion Institute, Paper 78-42 (1978).
- \* 3. Colket, M.B., Naegeli, D.W. and Glassman, I., "High Temperature Pyrolysis of Acetaldehyde", Int'l J. of Chem. Kinetics 7, 233 (1975).
- \* 4. Aronowitz, D. and Naegeli, D.W., "High Temperature Pyrolysis of Di-methylether", Int'l J. Chem. Kinetics 9, 471 (1977).
- \*\* 5. Hautman, D.J., Santoro, R.J., Dryer, F.L. and Glassman, I., "An Overall and Detailed Kinetic Study of the Pyrolysis of Propane", Int'l J. of Chem. Kinetics 13, 149 (1981).
- \*\* 6. Hautman, D.J., "Pyrolysis and Oxidation Kinetic Mechanisms for Propane", Princeton University Department of Mech. and Aero. Eng., Ph.D. Thesis, 1980.
- \*\* 7. Hautman, D.J., Dryer, F.L., Schug, K.P. and Glassman, I., "A Multiple Step Overall Kinetic Mechanism for the Oxidation of Hydrocarbons", Comb. Sci. and Tech. 25, 219 (1981).

- \* 8. Dryer, F.L. and Glassman, I., "High Temperature Oxidation of CO and CH<sub>4</sub>", 14th Symp. (Int'l) on Combustion, The Combustion Institute, Pittsburgh, PA, p. 987 (1973).
- \*\* 9. Santoro, R.J. and Glassman, I., "A Review of Oxidation of Aromatic Compounds", Comb. Sci. and Tech. 19, 161 (1979).
- \*\* 10. Euchner, J.A., "A Study of the Oxidation of Toluene in a Flow Reactor", Princeton University Department of Mech. and Aero. Eng., M.S.E. Thesis, 1981.
- \*\* 11. Euchner, J.A., Venkat, C., Brezinsky, K. and Glassman, I., "Preliminary Studies on the Oxidation of Aromatics at High Temperatures", 1st Int'l Specialists Meeting of the Combustion Institute, Bordeaux, France, July 1981.
- \*\* 12. Venkat, C., "High Temperature Oxidation of Aromatic Hydrocarbons", Princeton University Department of Chem. Eng., M.S.E. Thesis, 1981.
- \*\* 13. Venkat, C., Brezinsky, K. and Glassman, I., "High Temperature Oxidation of Aromatic Hydrocarbons", accepted for presentation and publication in 19th Symp. (Int'l) on Combustion.
- \*\* 14. Glassman, I., "Phenomenological Models of Soot Processes in Combustion Systems", AFOSR TR 79-1147 (1979).
- 15. Calcote, H.F., "Mechanisms of Soot Nucleation in Flames - A Critical Review", Comb. and Flame 42, 215 (1981).
- 16. Millikin, R.C., "Non-Equilibrium Soot Formation in Premixed Flames", J. Phys. Chem. 66, 784 (1962).

17. Schalla, R.L. and Hubbard, R.R., "Formation and Combustion of Smoke In Flames", in "Basic Considerations of Hydrocarbon Combustion", NACA Report 1300, Chap. IX (1959).
18. Street, J.C. and Thomas, A., "Carbon Formation in Premixed Flames, Fuel 34, 4 (1955).
- \* 19. Glassman, "Combustion", Academic Press, New York (1977).
20. Annual Book of ASTM Standards (1975), "Standard Method of Test for Smoke Point of Aviation Turbine Fuels", Designation D1322-75.
- \*\* 21. Yaccarino, P., "Parametric Study of Sooting Diffusion Flames", Princeton University Department of Mech. and Aero. Eng., M.S.E. Thesis, 1980.
- \*\* 22. Schug, K.P., Mannheimer-Timnat, Y., Yaccarino, P. and Glassman, I., "Sooting Behavior of Gaseous Hydrocarbon Diffusion Flames and the Influence of Additives", Comb. Sci. and Tech. 22, 235 (1980).
- \*\* 23. Glassman, I. and Yaccarino, P., "The Temperature Effect in Sooting Diffusion Flames", in 18th Symp. (Int'l) on Combustion, The Combustion Institute, Pittsburgh, PA, p. 1175 (1981).
- \*\* 24. van Teuren, K.W., "Sooting Characteristics of Liquid Pool Diffusion Flames", Princeton University Department of Mech. and Aero. Eng., M.S.E. Thesis, 1978.
- \*\* 25. van Teuren, K.W., Glassman, I. and Schug, K.P., "Sooting Characteristics of Liquid Pool Diffusion Flames", Paper No. 54, Eastern States/Combustion Institute Meeting, Miami Beach, Florida, Nov. 1978.

- \*\* 26. Glassman, I. and Yaccarino, P., "The Effect of Oxygen Concentration on Sooting Diffusion Flames", Comb. Sci. and Tech. 24, 107 (1980).
- \*\* 27. Glassman, I. and Lara, P.U., "The Temperature Effect in Sooting Premixed Flames", Paper No. 41, Eastern States Section/The Combustion Institute Meeting, Pittsburgh, PA, Oct. 1981.
- \*\* 28. Glassman, I., Brezinsky, K., Gomez, A. and Takahashi, F., "Physical and Chemical Kinetic Effects in Soot Formation", to be published in "Recent Advances in Aerospace Sciences", Plenum Press, New York (1982).

**V. STUDENT, POST-DOCTORAL, AND VISITOR TRAINING**

**A. Students and Present Location**

K.W. van Teuren, M.S.E., Officer U.S. Air Force

J.A. Eychner, M.S.E., ARCO Refining Co.

D.J. Hautman, Ph.D., EXXON Research and Engineering Co.

P. Yaccarino, M.S.E., General Motors Research Center

C. Venkat, M.S.E., Mobil Research and Development Co.

S. Murphy, current student

A. Gomez, current student

**B. Post-Doctoral Staff and Present Location**

Dr. R.J. Santoro, National Bureau of Standards

Dr. K.P. Schug, DFVLR, West Germany

**C. Visiting Faculty**

Prof. Y. Mannheimer-Timnat, Dept. of Aero. Eng., Technion, Israel

Institute of Technology

## VI. PUBLICATION INTEREST

Of the 28 references listed in Section IV, 22 were a result of AFOSR supported work and 18 were published during the 3 year period covered by this report. Of the 18, 7 were published in international archival journals or symposia volumes and 2 have been written and accepted for publication. An additional four manuscripts have appeared either as AFOSR reports or preprints of meetings papers.

Thus the results of the program have been widely disseminated. One report (Reference 14) has commanded wide interest and around 500 copies were requested and distributed. The requesters included Air Force laboratories such as Elgin and Wright-Patterson and practically every AF contractor working on the problem of soot particulate formation. The distribution of this and related work (References 22,23,25 and 26) has led to direct personal inquiries from aircraft and engine manufacturers such as Pratt and Whitney and McDonald-Douglas.

The overall model for aliphatic hydrocarbon oxidation has found use and successful application in catalytic combustor chamber (Princeton) general combustor models (PSI, SAI, Germany), and automobile engines (MIT, Milano). There indeed may be other applications that we are not aware.

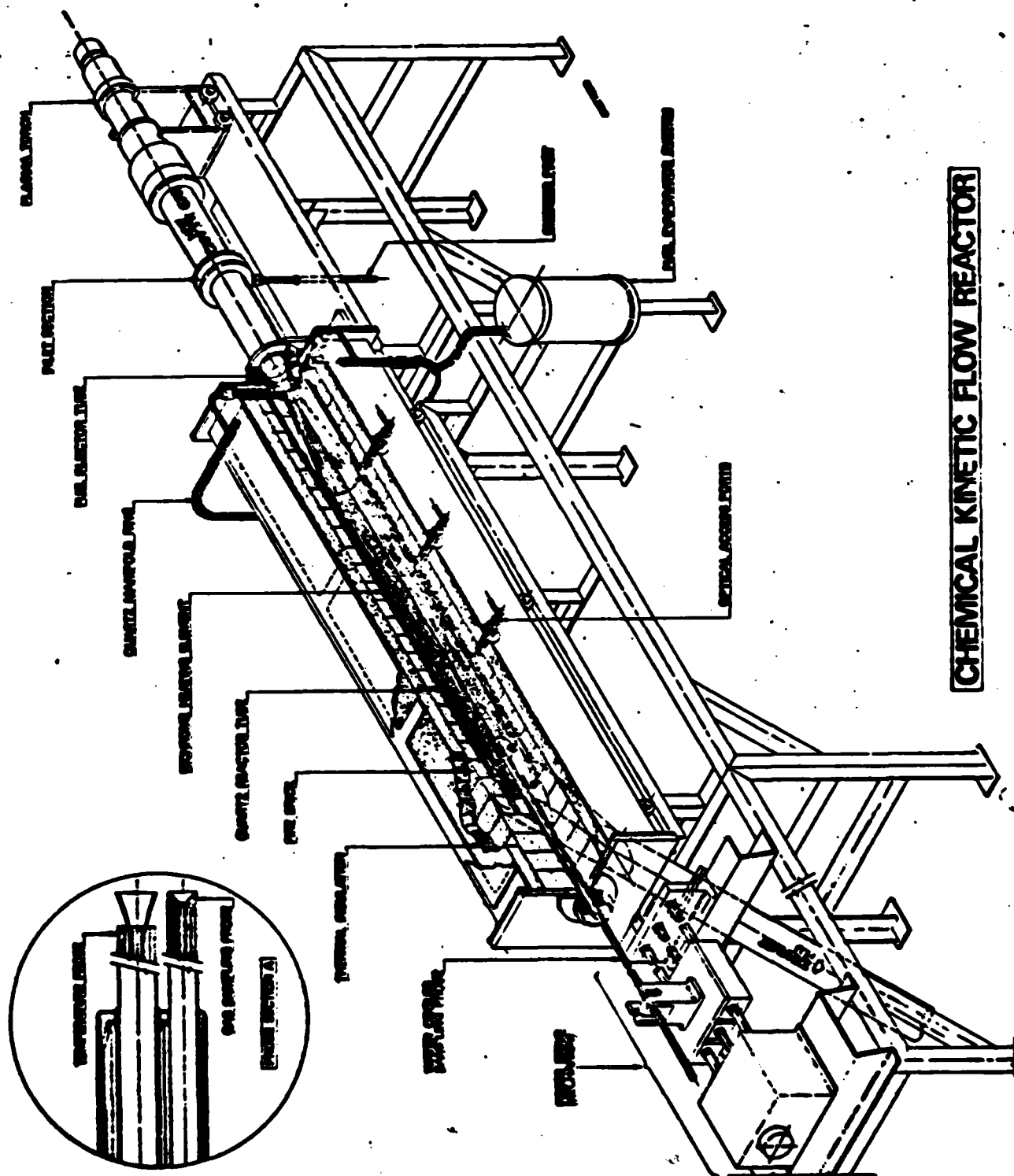
Similarly our work on aromatic oxidation has led to discussions with UTRC, GM, Mobil, EXXON and ARCO. Reference to our early work in this area has been numerous.

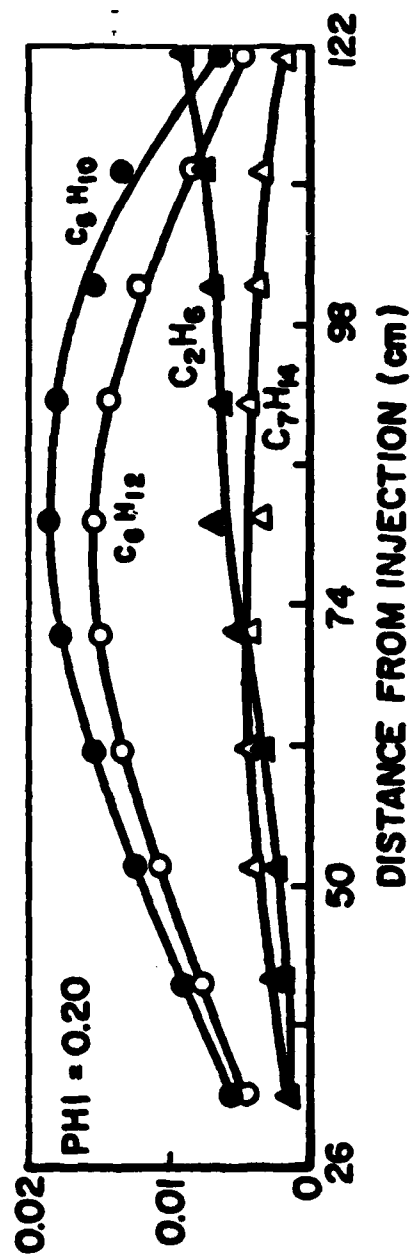
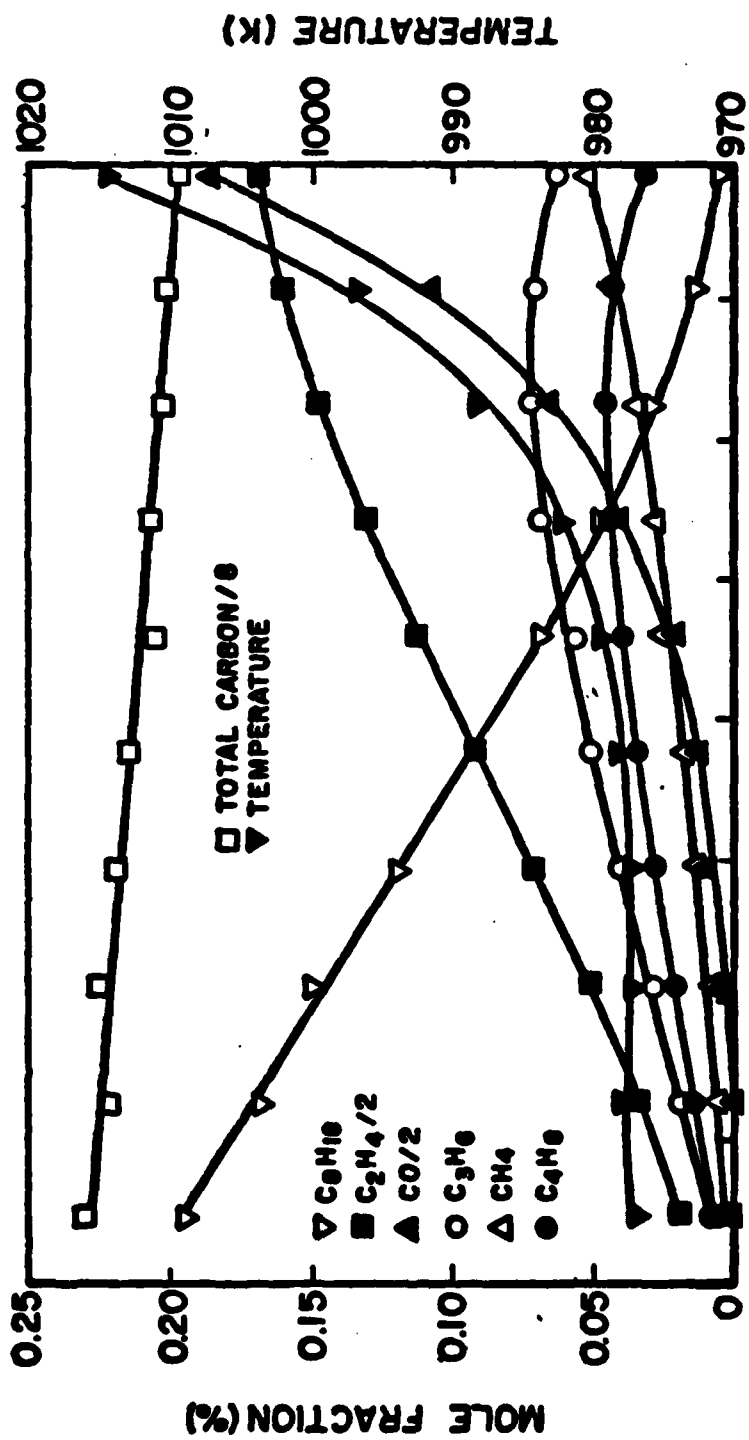
### List of Figures

1. Schematic of Princeton Turbulent Flow Reactor and Sampling Probe
2. Species Profiles for Lean ( $\phi = 0.20$ ) n-Octane Oxidation Noting Breakdown to Lower Olefins ( $C_2H_4$ ,  $C_3H_6$ ,  $C_4$ ,  $H_8$ )
3. Species Profiles for a Rich ( $\phi = 1.60$ ) Ethane Oxidation Noting the Formation of Acetylene ( $C_2H_2$ )
4. Experimental and Predicted Species Profiles and Temperature Rise for Lean Butane Oxidation
5. Species and Temperature Profiles for Lean ( $\phi = 0.36$ ) Oxidation of Benzene
6. Mass Flow Rate at the Diffusion Flame Sooting Height as a Function of Temperature Plotted in Arrhenius Form
7. Smoke Point Results of Liquid Fuel Mixtures. Note Non-linearity of Toluene Mixture
8. Ethylene Fuel Flow Rate at Sooting Height as a Function of Oxygen Index. Nitrogen as the Inert
9. Sooting Equivalence Ratio of Fuel-Oxygen-Nitrogen Mixtures as a Function of Temperature. x Points Denote Results for Air

# CHEMICAL KINETIC FLOW REACTOR

Figure 1





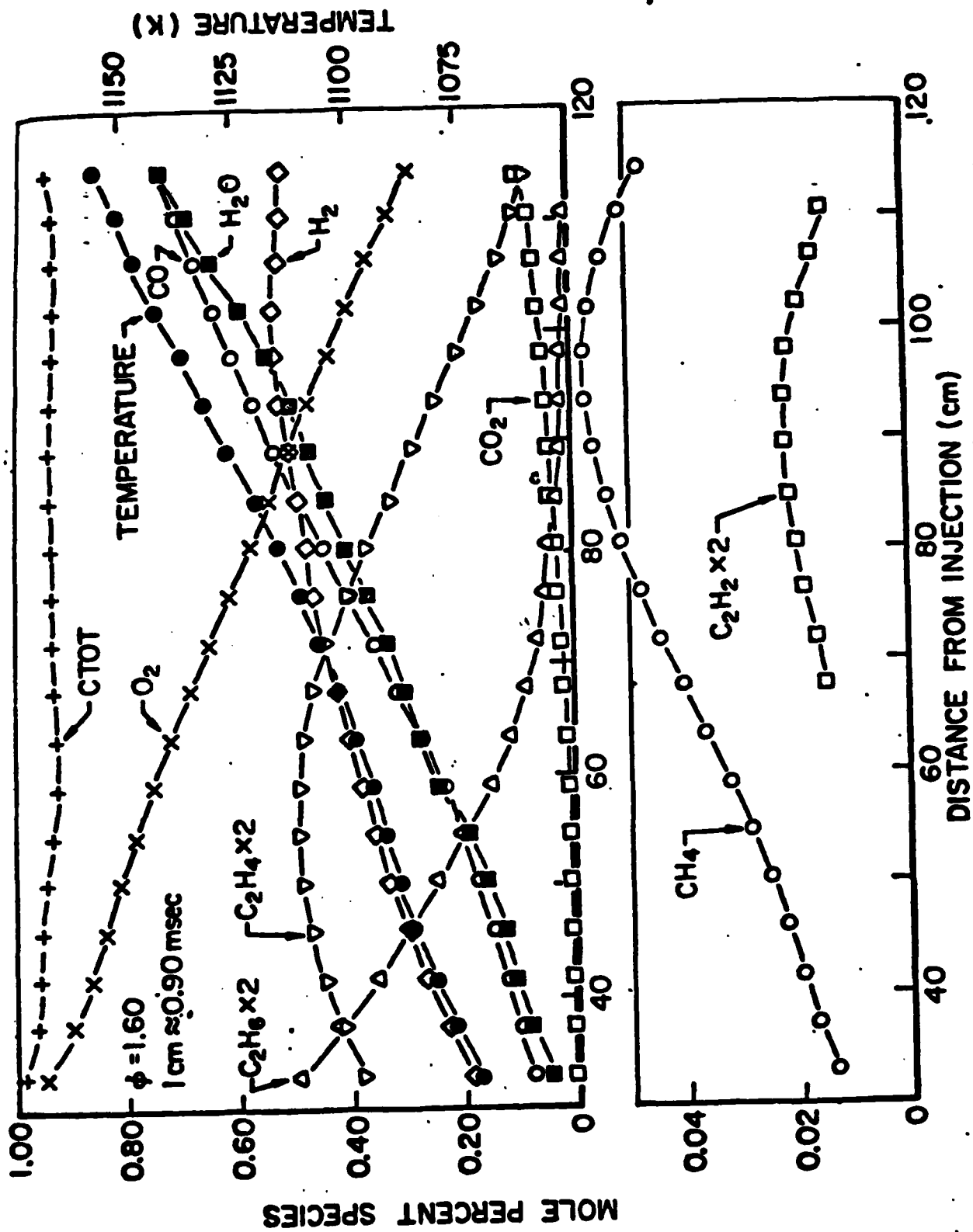


Figure 3

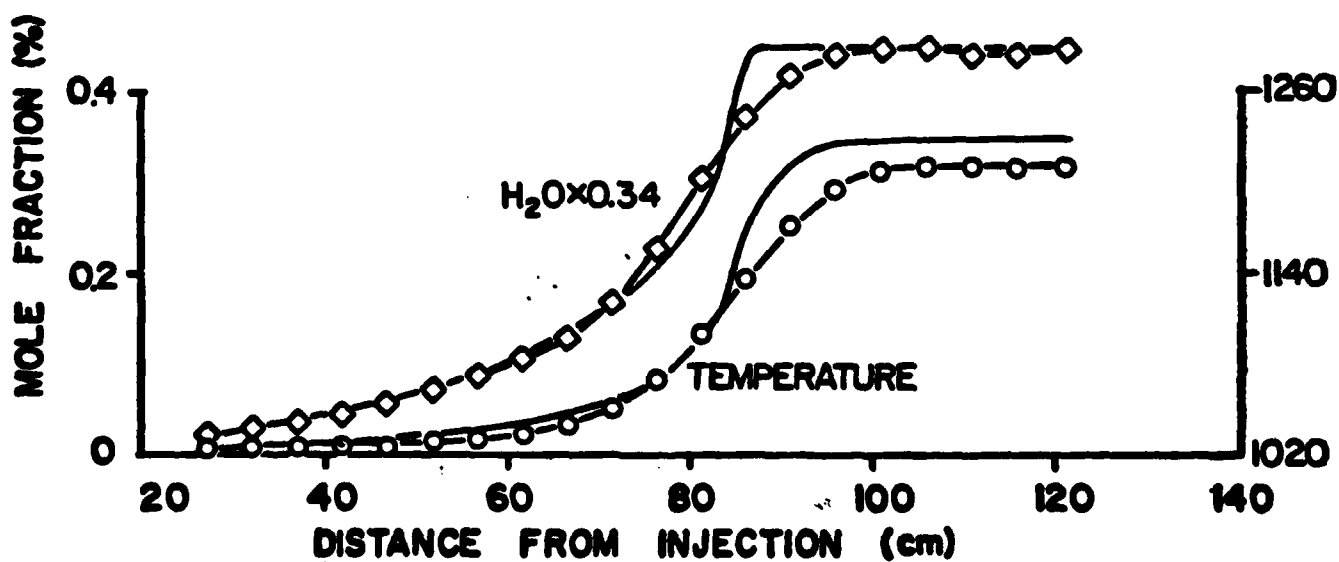
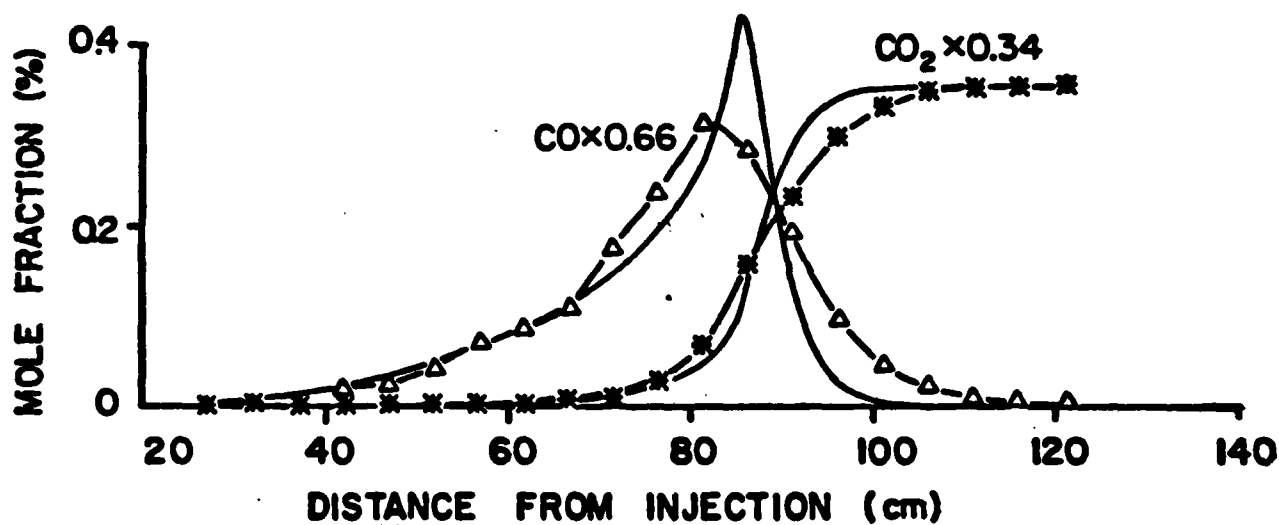
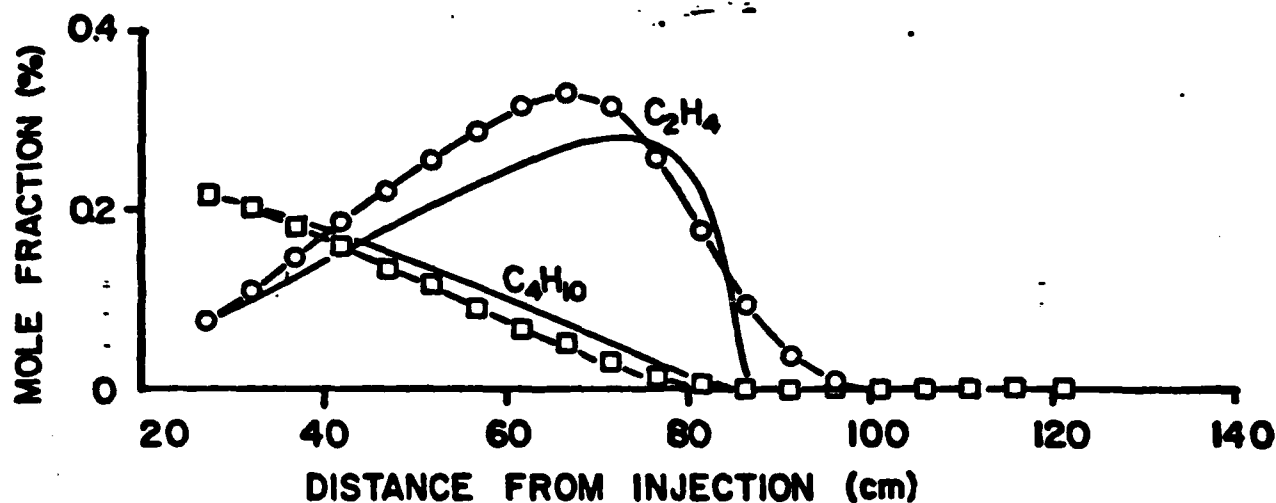
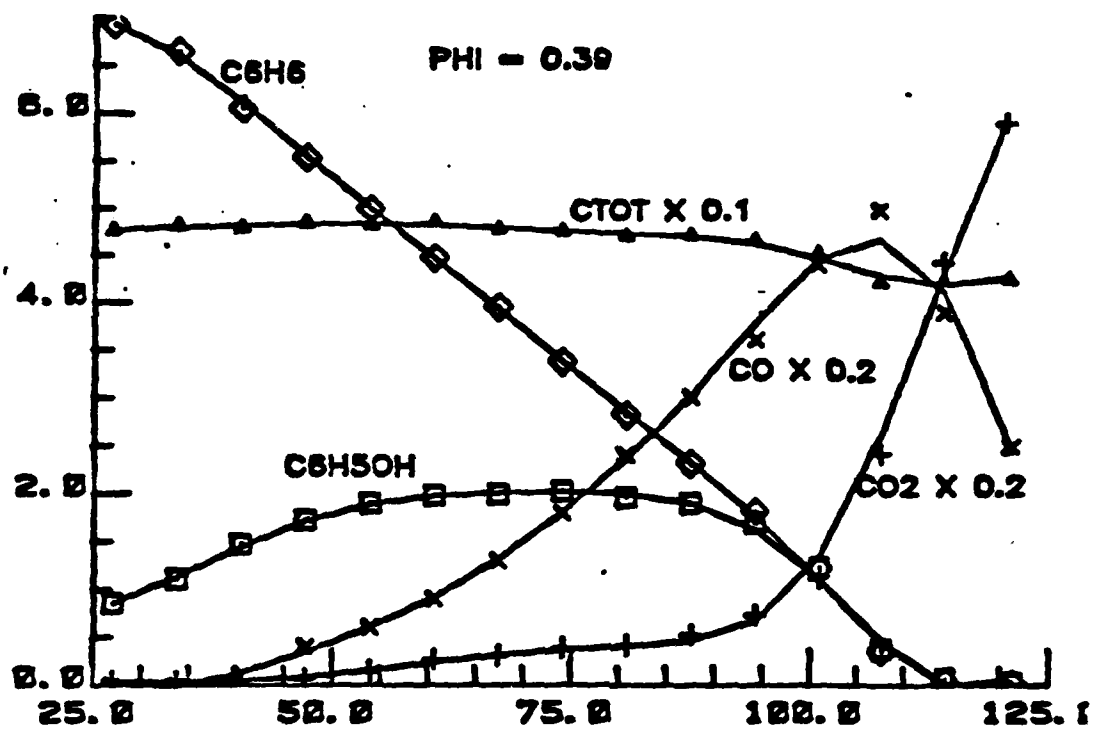


Figure 4

MOLE FRAC X E4



MOLE FRAC X E5

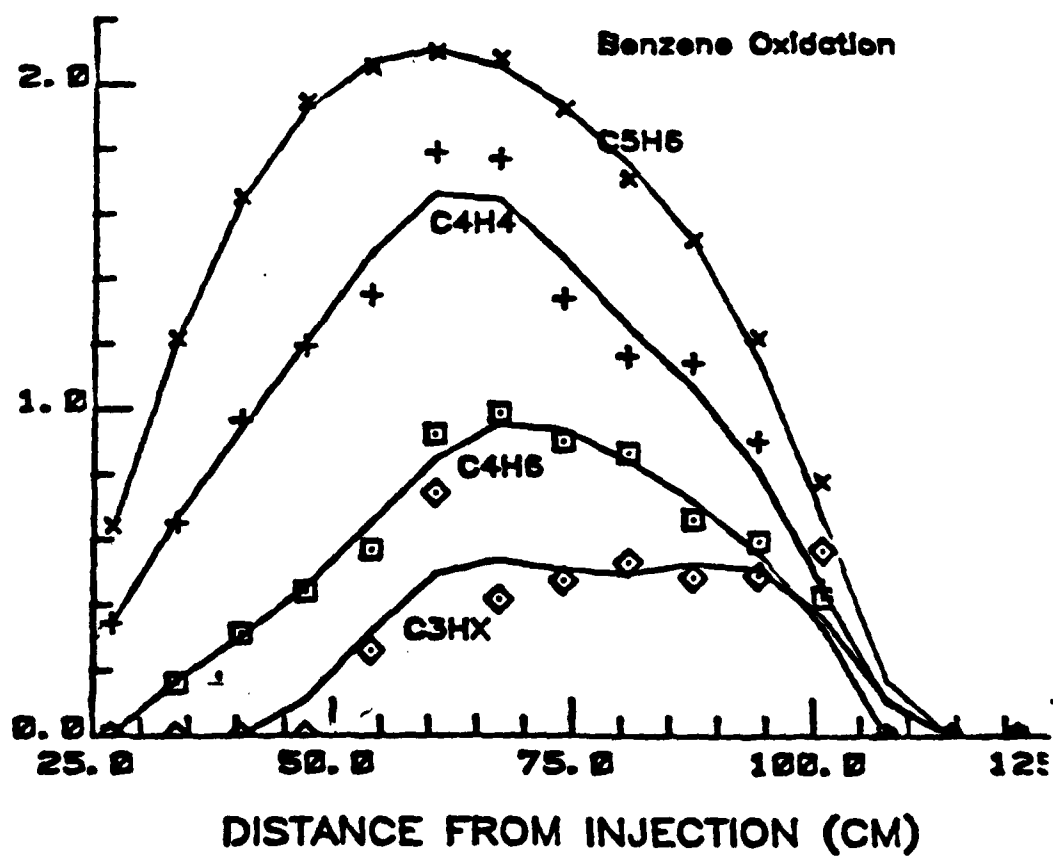


Figure 5

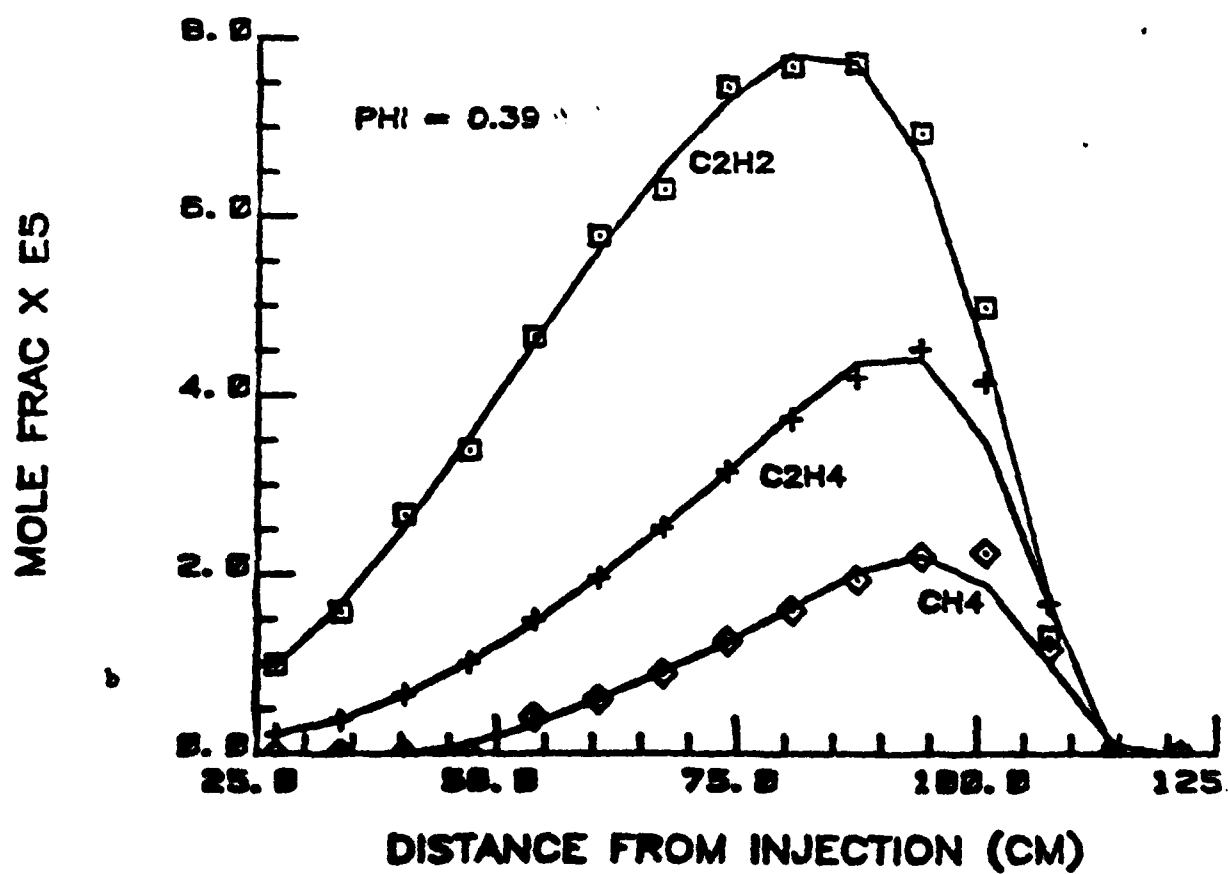
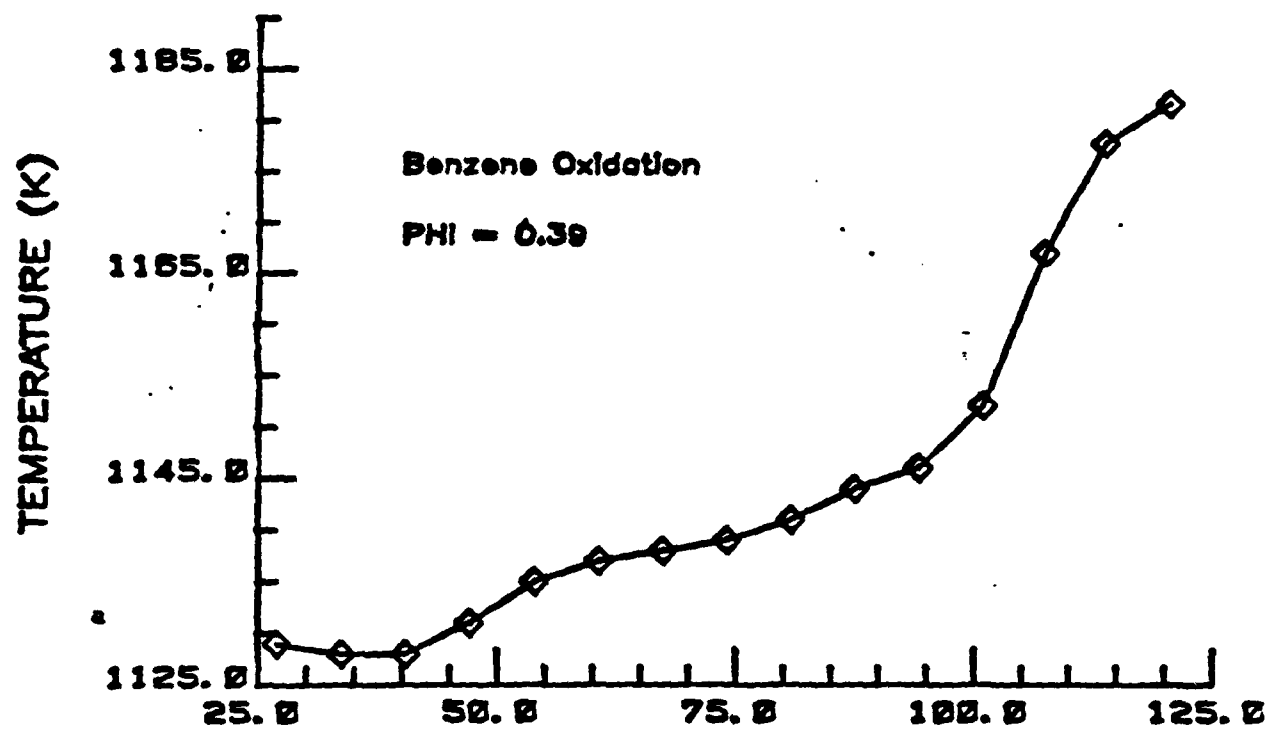


Figure 5

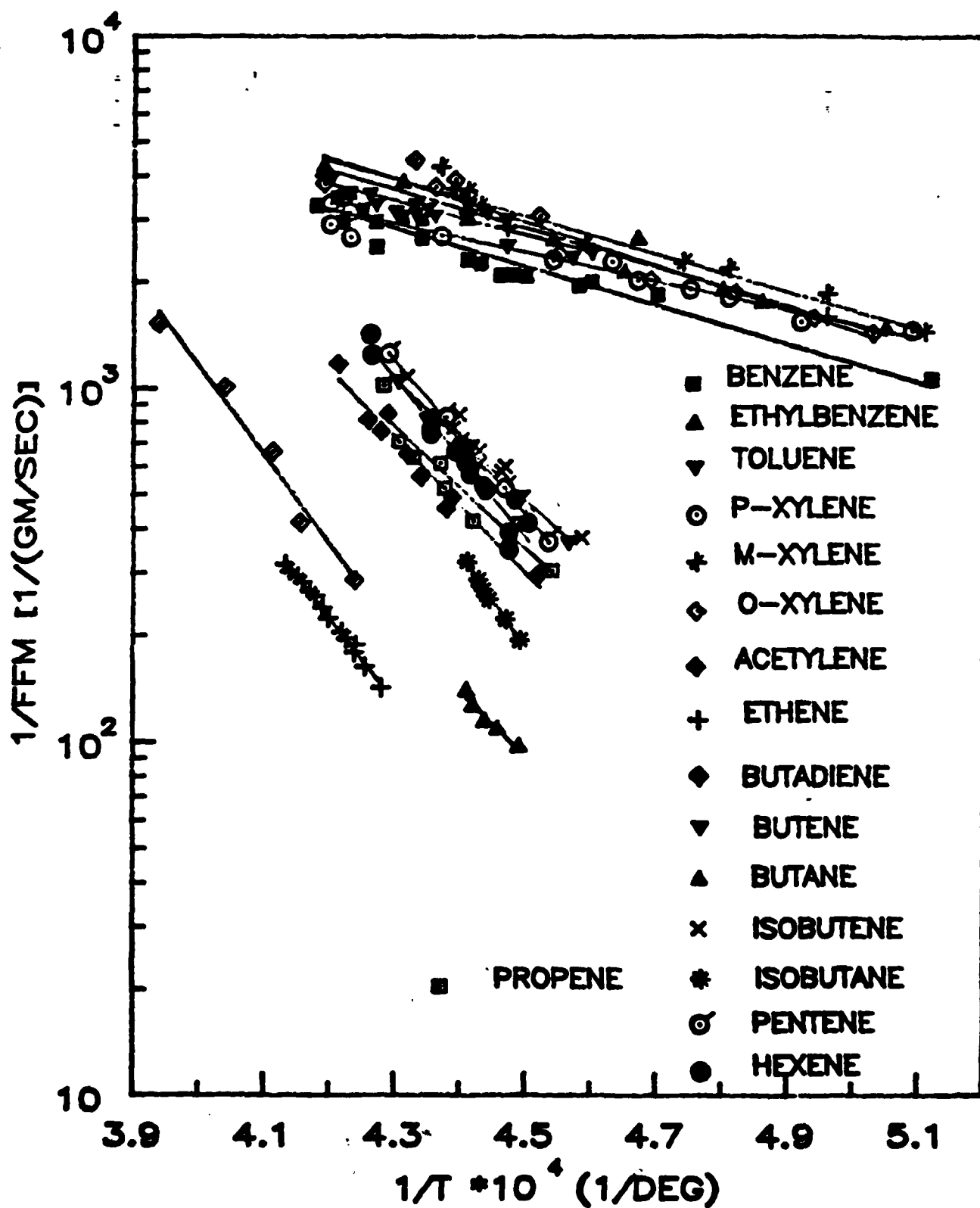


Figure 6

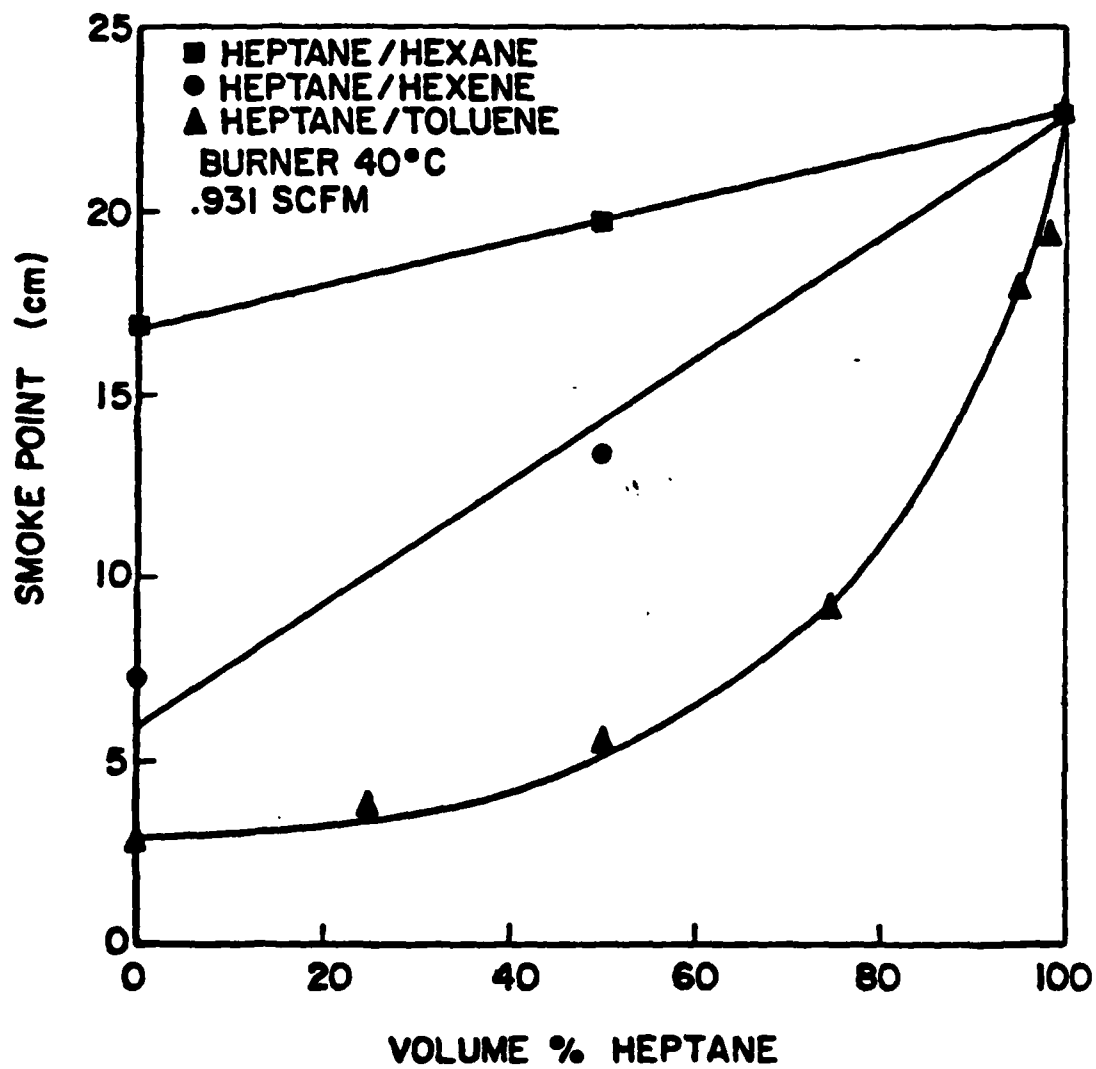


Figure 7

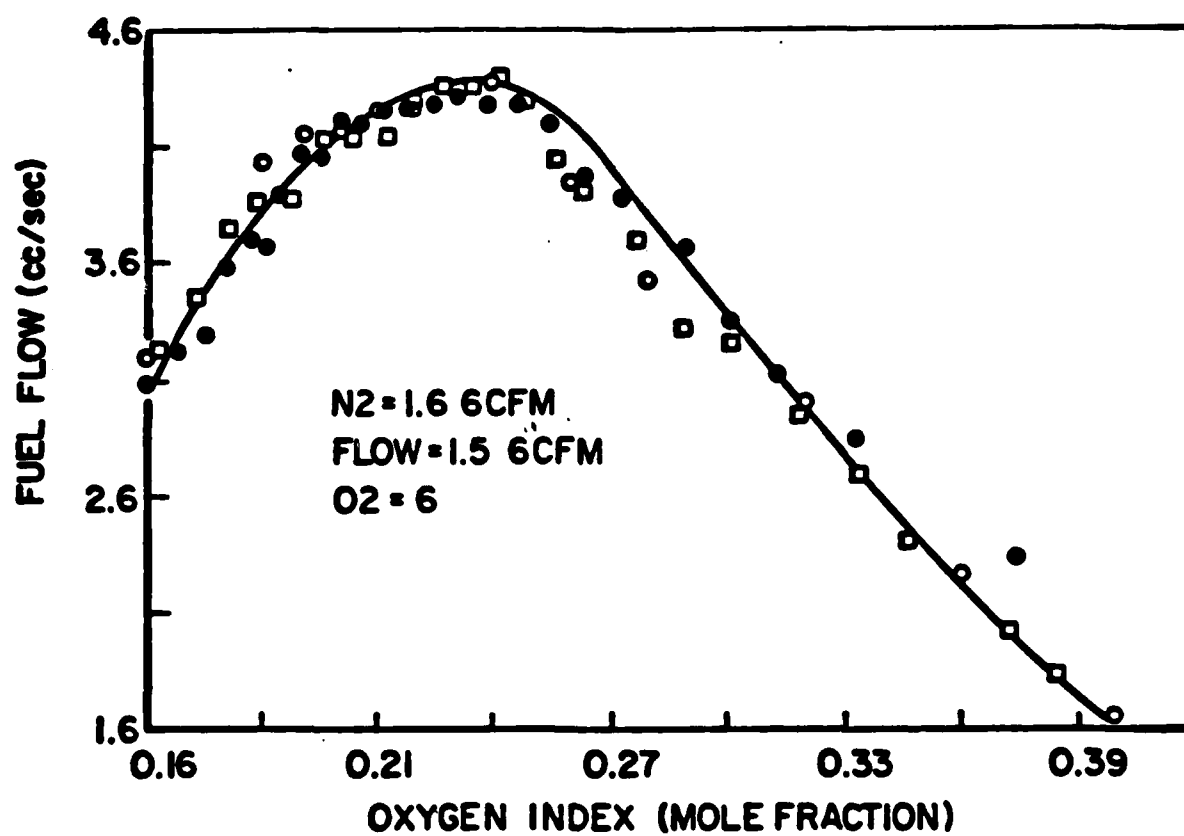


Figure 8

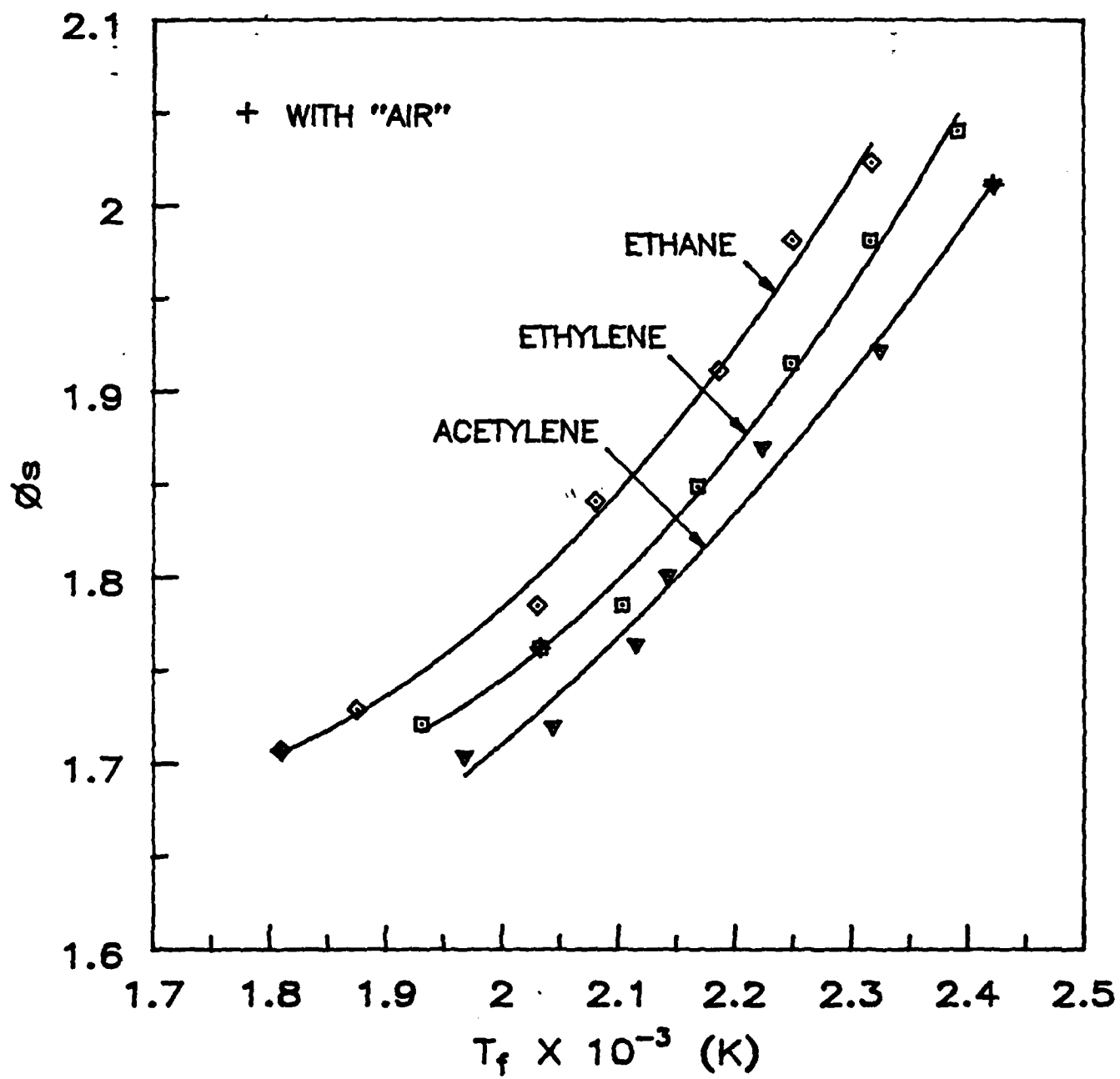


Figure 9

MED  
8